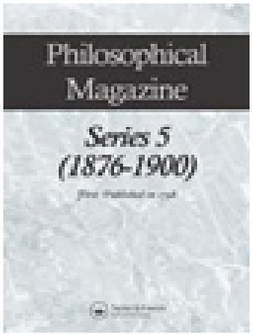

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XXIII. On a new law, analogous to those known under the names law of Avogadro and law of dulong and petit

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that the combination of sulphur with silver is assisted by radiation.

But it is not perhaps necessary to assume that the effective action of light is confined entirely to the surface of one of the electrodes. If, as is commonly believed, electrolytic conduction involves a series of decompositions and recompositions throughout the electrolyte, any cause which assists either the separation or recomposition (or both) of the components of the electrolyte might be expected to increase its conductivity; and it seems reasonable to suppose that the same influence which would assist the union of two substances when they have a tendency to unite would also be favourable to their separation when they have a tendency to separate. It is not impossible, therefore, that radiation, acting upon the surface of a thin layer of sulphide of silver through which an electric current is passing, might, by facilitating the molecular rearrangement of the atoms of sulphur and silver, exert a material influence upon the conductivity of the sulphide*.

So far as regards the explanation of the effect of light upon the resistance of selenium, I am aware that this paper contains little more than speculative suggestions, which are at present almost entirely unsupported by experimental evidence†. It is, however, noteworthy that these speculations led to the construction of a cell which, without containing a particle of selenium, behaved almost exactly as if it were composed of that substance. How far this may be considered to prove anything with regard to selenium I do not know; but in any case the discovery of another substance possessing the same remarkable property seems in itself to be a matter of some interest.

XXIII. *On a New Law, analogous to those known under the names Law of Avogadro and Law of Dulong and Petit.* By J. A. Groshans‡.

[Concluded from p. 30.]

IT may be said that, as yet, the study of the causes which influence the value of x has to be commenced, and that all that pertains to this constant is still uncertain. Still I

* There are some experimental reasons, into which I am not at present prepared to enter, for believing that the admixture with the sulphide of a certain amount of free sulphur is necessary for the development of sensitiveness to radiation.

† It is especially desirable to ascertain experimentally whether the combination of selenium with the metals used as electrodes in selenium cells is assisted by light.

‡ Communicated by the Author. Translated by W. W. J. Nicol, M.A., D.Sc.

may be permitted to embody in the following pages the principal observations that I have been able to make on this subject; and as in doing so I shall have frequently to refer to glycerine, it is perhaps as well to make a few remarks on its boiling-point.

There is but little agreement to be found among the figures given by various experimenters who have attempted to determine the boiling-point of this compound, $C_3H_8O_3$. The older experiments point to 9 as the value for x, the more recent to 9·5.

$$s\sqrt{9}=275{\cdot}1 \text{ and } s\sqrt{9{\cdot}5}=290{\cdot}1^*.$$

In this connection I may add that Wurtz's butylic glycol, $C_4H_{10}O_2$, boils at 183°–184°, that of Kekulé at 201°–204°:

$$s\sqrt{8{\cdot}5}=182{\cdot}9, \quad s\sqrt{9}=196^\circ{\cdot}2.$$

In the following table I have adopted 9 as the value of x for glycerine.

Glycerine exhibits a peculiar property with regard to x—it is this:—In glycerine, $C_3H_5(OH)_3$ one, two, or three of the hydrogens in hydroxyl groups may be replaced by ethyl, C_2H_5, to form ethylines. The original glycerine and its three derivatives form a species of homologous series the members of which have the common difference C_2H_4, and yet the increase of molecular weight is attended by a lowering of the boiling-point, exactly the opposite of what is observed in the case of other homologous series: this anomalous behaviour I attribute to the "*constancy of x*." In fact glycerine and its derivatives have all the same constant Tn/a, and consequently the same value of x—*i. e.* 9. The theoretical value of Tn/a, when $x=9$, is 83·41, as will be seen from the table. Other derivatives similar to the ethylic ones also possess the same constants.

TABLE XV.

Name of substance.	Formula.	a.	n.	S°, observed.	Tn/a.
Glycerine	$C_3H_8O_3$	92	14	277	83·69
Monoethyline	$C_5H_{12}O_3$	120	20	227	83·33
Diethyline	$C_7H_{16}O_3$	148	26	191	81·51
Triethyline	$C_9H_{20}O_3$	176	32	185	83·28
Triallyline.....	$C_{12}H_{20}O_3$	212	35	232	83·37

* Mendelejeff gives 290° at 760 millim.—W. W. J. N.

Methyl glycerine, $CH(OH)_3$, is not known, nor is methyl erythrite (methylphycite), $C(OH)_4$. But there are two compounds which have the composition of the ethylines of these two unknown bodies, and a third, which is the allyline of the former:—

(1) $C_7\ H_{16}O_3 = CH(OC_2H_5)_3$,

(2) $C_9\ H_{20}O_4 = C(OC_2H_5)_4$,

(3) $C_{10}H_{16}O_3 = CH(OC_3H_5)_3$.

And these have all the same value of Tn/a, $x=7$. This property (the constancy of x) is to be met with in very many other cases. I ought, however, to observe that in reality this constancy of x is but a special case. When substitution-products are formed each has a particular value of x, which may be the same as that of the body from which it was formed, or may be greater or less than that by one or more units, according to circumstances.

In instances where the value of x for the original substance cannot be determined, it is frequently found that the products of substitution, or some of them, have the same x. This is the case with urea, $CO(NH_2)_2$. According to Table I., the value of B is 12. Table XVI. contains four substituted ureas; $x=16$ in three cases, but in the fourth $=11$; or a difference of 5—a number which we shall find later on is a very frequent difference in the value of x for analogous bodies. In the following table I have, instead of the constant TB/a, inserted the value of x, $=1(27{\cdot}8)^2 \times (TB/a)^2$, which is the same thing, but in this instance more convenient. The boiling-points are the mean of those given in Fehling's dictionary.

TABLE XVI.

Name.	Formula.	A.	B.	S°, observed.	x, found.	x, calculated.
Urea	$CO(NH_2)_2$ ...	60	12			
Dimethyl urea ...	$CO(NHCH_3)_2$	88	18	269	15·90	16
Methylethyl urea.	$CO\begin{matrix}NHCH_3\\NHC_2H_5\end{matrix}$ ...	102	21	267	15·99	16
Diethyl urea	$CO(NHC_2H_5)_2$	116	24	263	15·91	16
Tetramethyl urea.	$CO(N(CH_3)_2)_2$	116	24	176	11·16	11

In the last column of the table is given the theoretical value of x, which is simply the whole number nearest to the found

value. In Table XVII. the constancy of x is given in the case of the hydrazines, bodies resembling in formulæ urea; and the hypothetical first member, N_2H_4, differs from that in the ureas, CON_2H_4, by the group CO.

TABLE XVII.

Name.	Formula.	A.	B.	S°, observed.	x, found.	x, theory.
Hypothetical first member	NH_2 NH_2	32	10			
Phenyl hydrazine	NHC_6H_5 NH_2	108	20	233	11·36	11
Diethyl hydrazine ...	NHC_2H_5 NHC_2H_5	88	22	96·5	11·10	11
Phenylmethyl hydrazine...	NHC_6H_5 $NHCH_3$	123	23	223	11·13	11

Here, again, is the value of $x=11$, as was the case in one of the bodies in the last table*.

Table XVIII. contains ethylene diamine, $C_2H_4N_2H_4$, and its substitution-products, along with an analogous compound,

TABLE XVIII.

Ethylene diamine and its substitution-products.

Formula.	a.	B.	S°, observed.	x, found.	x, calculated.
$N_2H_4(C_2H_4)$	60	16	117	13·99	14
$N_2H_2(C_2H_4)_2$.....	86	20	170	13·73	14
$N_2(C_2H_4)_2(C_2H_5)_2$	142	32	185	13·72	14
$N_2(C_2H_4)_3$	112	24	210	13·86	14
$N_2(C_2H_4)_3$	103	26	208	19·07	19

* We find in the aromatic series bodies metameric with those in Table XVII.; thus:—

Metamers of $C_6H_8N_2$.

Three phenylene diamines, with the constants x respectively =12, 13, 14.

Metamers of $C_7H_{10}N_2$.

Three cresylene diamines, with x respectively 14, 13, and 14.

In ammonia, NH_3, $x=9$; and thus we find that in the three series of bodies of which the three following are types there is a steady increase of x apparently without limits:—

Ammonia, NH_3, ... $x=9$,

Ethylene diamine, $N_2C_2H_8$, . $x=14\frac{5}{5}$,

Triethylene triamine, $N_3C_4H_{13}$, $x=19$;

the difference NC_2H_5 therefore corresponds to $x=5$, or in the atomic weight $=43$, in density numbers $=10$, numbers comparable with those observed in the case of the elements (see above).

It is also possible to use the property of *the constancy of x in substitution-products* to determine the value of some density-numbers, especially that of chlorine. It is found that, in general, x does not change when 1, 2, 3, or more atoms of chlorine are substituted for 1, 2, 3, or more atoms of hydrogen in a body of the formula $C_pH_qO_r$. Table XIX.

TABLE XIX.

Toluol and its Chlorine substitution-products.

Formula.	*a*.	B.	S°, observed.	T. B/*a*.
C_7H_8	92	15	108 N	62·1
C_7H_7Cl	126·5	18	164 L	62·18
$C_7H_6Cl_2$.....	161	21	206 W	62·48
$C_7H_5Cl_3$.....	195·5	24	237 L	62·61
$C_7H_4Cl_4$.....	230	27	255 L	61·98

N=Noad; L=Limpricht; W=Wicke.

shows this clearly in the case of the four chlorine derivatives of toluol, C_7H_8; for when the density-number of chlorine is taken as 4, the value of the constant Tn/a is all through 62·2, and x is equal to 5. In the case of benzol, C_6H_6, $x=4$, and so also for C_6H_5Cl, $C_6H_4Cl_2$, and $C_6H_3Cl_3$; while $x=4·5$ for $C_6H_2Cl_4$ and C_6HCl_5. But $=5$ for C_6Cl_6.

I have published, elsewhere*, extended tables showing clearly this constancy of x in chlorine substitution-products.

* *Annalen*, Wiedemann, 1879, p. 134; J. A. Groshans, *Ein neues Gesetz*, Leipzig, Barth, 1882, p. 43; J. A. Groshans, *De la nature des Eléments*, Haarlem, héritiers Loosjes, 1875, p. 47.

It follows from this that numerous analogous compounds have the same value for x. In the following examples I have, for the sake of conciseness, omitted the numerical data, giving only the value of x deduced from the observed boiling-points :—

Examples of the Constancy of x.

(α) Methylic and Ethylic compounds, with Oxygen, Sulphur, Selenium, and Tellurium.

$(CH_3)_2O$,	$x=3$.	$(C_2H_5)_2O$,	$x=5$.
$(CH_3)_2S$,	$x=3$.	$(C_2H_5)_2S$,	$x=5$.
$(CH_3)_2S_2$,	$x=3$.	$(C_2H_5)_2S_2$,	$x=5$.
$(CH_3)_2Se$,	$x=3$.	$(C_2H_5)_2Se$,	$x=5$.
$(CH_3)_2Te$,	$x=3$.	$(C_2H_5)_2Se_2$	$x=5$.

x in every case $=m$.

(β) Analogous compounds of Carbon and Silicon.

CCl_4,	$x=2$.		
$SiCl_4$,	$x=2$.	$(CH_3)_4C$	$x=6$.
$CHCl_3$,	$x=2$.		
$SiHCl_3$,	$x=2$.	$(CH_3)_4Si$,	$x=6$.

Here again $x=m$.

(γ) Analogous compounds of the members of the *triad*, Phosphorus, Arsenic, and Antimony.

$(CH_3)_3P$,	$x=5$.	$PO(C_2H_5O)_3$,	$x=7$.
$(CH_3)_3As$,	$x=5$.	$AsO(C_2H_5O)_3$,	$x=7$.
$PO(CH_3O)_3$,	$x=5$.	PI_3,	$x=7$.
$AsO(CH_3O)_3$	$x=5$.	SbI_3,	$x=7$.

$x=7$, also for $HgCl_2$, $HgBr_2$, HgI_2, and Hg_2I_2.

On the Temperatures T $(273°+S°)$ *considered as proportional to the Molecular Volumes of Substances in the Gaseous State at the Boiling-point* S°.

We are accustomed to regard the absolute boiling-points as quantities expressing degrees of heat, and this no doubt they are ; but they are at the same time proportional to the molecular volumes of the vapours, analogous to those of the liquids at the boiling-point ($v_s=a/d_s$). When the vapour-density D_s is expressed in terms of the volume of a gram of water at 4° C., the absolute boiling-point T (affected by a

constant coefficient) expresses the volume in cubic centimetres of the molecular weight in grams.

In explaining this I may be permitted to restate a few well-known facts.

Two grams of hydrogen at 760 millim., and at 0° C., occupy 22327 cubic centim.

a grams of any substance in the state of gas under the same conditions of temperature and pressure also occupy 22327 cubic centim., both by convention and in accordance with Avogadro's law.

This constant volume 22327 cubic centim. is multiplied at the boiling-point S° by the fraction T/273; and consequently the volume (molecular) of a substance in vapour at its boiling-point is

$$v_s = 22327\ T/273 = 81{\cdot}8\ T \text{ cubic centim.},$$

and the vapour-density is

$$D_s = a/v_s = a/81{\cdot}8\ T.$$

As the coefficient 81·8 is the same for all bodies, it may be omitted if it be thought fit to do so.

Relation between the Gaseous Molecular volume V_s *and the Liquid Molecular volume* v_s.

When we take equal volumes (*e.g.* cubic centims.) of different liquids at S° and convert them into vapour by heating, we obtain a certain number of cubic centim. of vapour at 760 millim. and at S°; this number is for any substance whatever.

$$81{\cdot}8\ T/v_s \text{ (cubic centim.)}.$$

In this connection I wish to draw attention to a special case which appears of particular interest: it is as follows:—

We find that in certain groups of analogous substances

$$81{\cdot}8\ T/v_s = \text{constant}.$$

This phenomenon is independent of the new law, and may be expressed as follows:—

$$V\frac{273}{T} = \text{constant} = v_r.$$

(The constant 81·8 is omitted here.)

I shall call the constant v_r the "reduced volume" of the substances in question.

When a cubic centimetre at *s*° of the liquids (which have the same v_r) is volatilized, one obtains a definite volume of vapour which is the same for all these substances, and is

$$\text{vol. const.} = 22327/v_r \text{ cubic centim.}$$

Table XX. gives the value of v_r for some groups of these substances, and also the volumes (constant) of vapour.

TABLE XX.

Name.	Formula.	v_s.	S°, observed.	Authority.	v_r.	c. c. of vapour.
Toluol	C_7H_8	119·57	108	No.	85·7	260
Methyl benzoate ...	$C_8H_8O_2$	151·46	199	Pe.	87·7	255
Methyl salicylate ...	$C_8H_8O_3$	157·23	223	Kp.	86·5	258
Ether	$C_4H_{10}O$	105·97	35		93·9	238
Ethyl carbonate ...	$C_5H_{10}O_3$	140·56	126	Kp.	96·2	232
Ethyl propionate ...	$C_5H_{10}O_2$	128·08	100		93·7	238
Ethyl valerate	$C_7H_{14}O_2$	176·53	143	Kp.	115·8	193
Ethyl succinate.....	$C_8H_{14}O_4$	209·71	217	Kp.	116·8	191

No=Noad; Pe=Peligot; Kp=Kopp.

It is clear that the phenomenon of the constancy of vr points to equality at the same time of the constants Tn/a and v_sn/a; whence it follows that

$$\frac{v_s}{v'_s} = \frac{T}{T'}.$$

Here is another consequence of the above :—

Since it has been shown that the law of density numbers is applicable to the volumes of vapour T and T′ of compounds, it must also be applicable to the liquid volumes v_s and v'_s.

Application of the New Law to Volumes of Liquids at their Boiling-points.

The properties of the liquid volumes are different from those of the gaseous volumes. These last, when of isomeric bodies, can differ greatly; the former, on the other hand, are equal, or almost exactly so. But it seems to me a little premature to make any extended remarks on the subject of liquid volumes in general.

If d_s be the density of any liquid whatever at the boiling-point S°, the volume $v_s = \frac{a}{d_s}$; and in applying the law to these volumes we obtain the constants v_sn/a analogous to Tn/a (this constant v_sn/a or v_sB/a is the same as n/d_s or B/d_s). Instead of writing v_sn/a, I shall write k_s, which is more convenient. The following Table contains three groups, each of three members from Tables XIX. and XX. I have not been able to form larger groups, comprising 8–10 compounds, for the data relating to the volumes of liquids are too scanty.

TABLE XXI.

Names.	Formula.	*a.*	*n.*	Volume observed.	Observers.	k_s.
Ether	$C_4H_{10}O$	74	15	106·1	Kp.	21·51
Ethyl propionate ...	$C_5H_{10}O_2$	102	17	128·1	We.	21·34
Ethyl carbonate ...	$C_5H_{10}O_3$	118	18	138·8	Kp.	21·17
Toluol	C_7H_8	92	15	119·5	Lo.	19·49
Methyl benzoate ...	$C_8H_8O_2$	136	18	136·2	Kp.	19·89
Methyl salicylate ...	$C_8H_8O_3$	152	19	152·2	Kp.	19·63
Propylic oxide	$C_6H_{14}O$	102	21	151·6	Za.	31·21
Ethyl valerate	$C_7H_{14}O_2$	130	23	173·5	Kp.	30·70
Ethyl succinate.....	$C_8H_{14}O_4$	174	26	209·0	Kp.	31·23

Kp.=Kopp; We.=Weger; Lo.=Longuinine; Za.=Zander.

Table XXII. contains several substitution-products resulting from the action of chlorine, bromine, and iodine on the alcohols and fatty acids.

TABLE XXII.

Name.	Formula.	*a.*	*n.*	v_s observed.	Observers.	k_s.
		m=2.				
Methyl alcohol	CH_4O	32	6	42·2	Kp.	7·91
Methyl bromide ...	CH_3Br	65	13	58·2	Pi.	7·96
Methyl iodide	CH_3I	142	18	68·3	Pi.	8·66
		m=3.				
Ethyl alcohol	C_2H_6O	46	9	62·0	Kp.	12·12
Ethyl chloride	C_2H_5Cl	64·5	11	71·2	Pi.	12·14
Ethyl bromide	C_2H_5Br	109	16	78·4	Pi.	11·51
Ethyl iodide	C_2H_5I	156	21	86·1	Pi.	11·59
		m=4.				
Propyl alcohol	C_3H_8O	60	12			
Normal	.....	.....	.....	81·3	Za.	16·28
Iso-	.....	.....	.....	82·7	Za.	16·59
Propyl chloride ...	C_3H_7Cl	78·5	14			
Normal	.....	.....	.....	91·6	Za.	16·40
Iso-	.....	.....	.....	93·8	Za.	16·78
Propyl bromide ...	C_3H_7Br	123	19			
Normal	.....	.....	.....	97·4	Za.	15·03
Iso-	.....	.....	.....	99·4	Za.	15·36
Propyl iodide	C_3H_7I	170	24			
Normal	.....	.....	.....	107·2	Za.	15·13
Iso-	.....	.....	.....	108·7	Za.	15·34
		m=6.				
Amyl alcohol.....	$C_5H_{12}O$	88	18	124·4	Kp.	25·45
Amyl chloride	$C_5H_{11}Cl$	106·5	20	137·0	Kp.	25·73
Amyl bromide	$C_5H_{11}Br$	151	25	149·2	Pi.	24·70
Amyl iodide	$C_5H_{11}I$	198	30	158·8	Kp.	24·06

Kp.=Kopp; Pi.=Pierre; Za.=Zander.

On the Variability of Physical Properties.

I have given the above name to the following phenomena:—

One frequently finds differences (according to Kopp reaching sometimes as much as 2 per cent.) in the density of the same substance at the same temperature. Similar differences are to be observed in the fusing- and boiling-points. Such differences present themselves when these physical properties have been determined by different persons or by the same observer at different times.

Space does not permit me to cite more than a very few instances.

I shall begin with crotonic acid, $C_4H_6O_2$; $a=86$, $n=12$. According to the law of density-numbers, and in consonance with analogy (which I need not further refer to), this acid should have the value of Tn/a corresponding to $x=5$, that is, the same constant as that of water.

There are three known isomers of this substance, which differ in chemical properties, with which I need not trouble my readers. One of these isomers, β, or isocrotonic or quartenylic acid, has the following physical properties; it is a liquid, not solidifying even at $-15°$ C., and boiling at 171°–173°; from $S°\sqrt{5}$ is calculated 172°·5. There is thus complete concordance between the calculated and observed boiling-point.

With regard to the other isomers, their physical properties, as given in Fehling, are as follows:—

(1) *a.* acid—solid crotonic acid, tetracrylic acid: melting-point 71°–72°, boiling-point 187° (corr.).

(2) Metacrylic acid: melting-point +16°, boiling-point 160°·5.

We have seen above that the β or iso-acid has $x=5$. For its two isomers we find respectively $x=5{\cdot}330$ and $x=4{\cdot}734$; the mean value is $x=5{\cdot}03$, which is essentially the same as $x=5$.

The particular fact that suggested to me the idea of the mean value for x in various isomers was as follows:—

"The liquid acid, which does not solidify even at $-15°$, is changed, by heating to 180° in a sealed tube, into the solid modification melting at 71°·5 and boiling at 187°"*.

We may infer from this that the physical properties depend, among other things, on the treatment to which the compound has been subjected.

* Wurtz, *Dict. Suppl.* p. 551.

In this connection I shall take some other case from the paper by Thorpe on the molecular volumes of liquids, Chem. Soc. Journ. 1880.

Properties of the Compounds Br_2 *and* ICl.

The molecular weights of the above substances are respectively 160, 162·5, being very nearly equal, and both have B=18. We would expect to find their densities (at the boiling-points) equal, but they differ by 0·1, or about 3·5 per cent. With regard to their densities at 0°C, δ_0, these are practically equal, notwithstanding the fact that their boiling-points differ by 42°. The following are the data relating to the above :—

	a.	B.	S°.	*x.*	d_0.	d_s.
Br_2	160	18	59·3	1·81	3·1883	2·9822
ICl	162·5	18	101·5	2·22	3·1822	2·8812

The values of x differ from the whole number 2 : the one is smaller, the other greater, the mean being $x=2·01$. Where $x=2$ for each body the respective boiling-points would be 76°·5 and 81°·9, which lie close together ; and the two densities d_s and $d'_{s'}$ would have been equal. I have calculated from the dilatations observed by Thorpe, what the densities would be at the calculated boiling-points : they are respectively 2·9244 and 2·9404.

It appears, then, that there exist in the case of these substances certain unknown causes which affect the boiling-points, raising the one 19°·4 and lowering the other 17°·5.

The existence of such an influence in very many cases will be strange to no one, for it has been suspected by many. It is the new Law, however, that points most clearly to it.

This also explains why the values of x, calculated from observed boiling-points, do not always present themselves as whole numbers, but are often affected by fractions, for instance :—

I have for valid reasons assumed that $x=3$ in the case of the four following bodies (see above) :—

C_2H_6S . . $x=3·28$. $C_2H_6S_2$ . . $x=3·12$.

C_2H_6Se . . $x=3·05$. C_2H_6Te . . $x=3·27$.

The experiments of Thorpe (*loc. cit.*) furnish yet another example.

Properties of the Substances S_2Cl_2 *and* SO_2Cl_2.

These two bodies have the same molecular weight, the density-number is the same, = 12. The data are as follows:—

	a.	B.	S° obs.	*x* obs	d_0.	d_s.
S_2Cl_2	135	12	138·1	1·73	1·7094	1·4920
SO_2Cl_2	135	12	69·9	1·20	1·7081	1·5602

Mean . . $x = 1{\cdot}46$.

The boiling-points differ by 68°·2, but the almost perfect equality of the two densities d_0 points to the equality of x; and we may admit that the true mean value is $x = 1{\cdot}5$, which gives 110°·1 as the common boiling-point.

In the two sets of cases that we have examined above, it appears that the disturbing cause does not operate till above 0°C., the values of d_o are the same in each pair. But this is not always the case: for instance, in two isomers examined by Thorpe (*loc. cit.*),

	a.	B.	S° obs.	*x* obs.	d_0.	d_s.
$C_2H_4Cl_2$	99	14	83·5	3·28	1·2808	1·1563
$C_2H_4Cl_2$	99	14	59·9	2·86	1·2309	1·1092

Mean . . $x = 3{\cdot}07$. $s\sqrt{3} = 67{\cdot}5$.

Such a disturbing influence on the boiling-points and densities of liquids is of a nature to hinder the progress of the study of the physical properties of substances.

Compounds Liquid at the Ordinary Temperature.

The best method of applying the law of density-numbers to liquids is perhaps that based, as above, on the comparison of the volumes at the boiling-points; but the data necessary for this comparison are but seldom available. When this is the case, we are still able in very many cases to verify the density-numbers simply by comparing together the values of d_o or d_t (t being the ordinary temperature 15°—20°C.) of analogous bodies, when the values of k_t will exhibit an agreement more or less complete.

In Table XXIII. an example is given of the above. The substances are arranged in the order of their boiling-points. By thus employing corresponding temperatures (slightly raised), it is possible to obtain satisfactory concordance in the values of k. When $t = 0$ the constants k_t arrange them-

TABLE XXIII.

Formula.	S°obs.	B.	d_t.	$t°$.	k_t.
$C_6H_{15}As$.....	140	29	1·151	16·7 (1)	25·20
$C_6H_{15}Sb$.....	158·5	34	1·3244	15 (1)	25·67
$C_6H_{15}O_3As$...	167	32	1·224	0 (2)	26·14
$C_6H_{15}O_3P$ ...	191	27	1·075	0 (3)	25·12
$C_6H_{15}O_4P$ ...	215	28	1·086	0 (4)	25·78
$C_6H_{15}O_4As$...	236	33	1·3264	0 (2)	24·88

(1) Landolt; (2) Crafts; (3) Williamson; (4) de Clermont.

selves in the contrary order to that of the points of ebullition S°.

I have thought it interesting to compare with the above six compounds another, the formula of which resembles those of the bodies in the table: this is $((C_2H_5)_3Sn)_2$. Its properties are as follows:—

	S°obs.	B.	d_0.	k_0.
$C_{12}H_{30}Sn_2$ . .	237° (Ca.)	70	1·4115 (La.)	49·59.

Ca = Cahours; La = Ladenberg, who has found S = 267°.

We have thus for

$$C_{12}H_{30}Sn_2 \quad . \quad . \quad k_0 = 2 \times 24{\cdot}79,$$
$$C_6H_{15}O_4As \quad . \quad . \quad k_0 = 24{\cdot}88,$$

A most complete agreement.

The value of k_t for liquids appears to depend on the value of p and q in the general formula $C_pH_qO_r$, for, as seen above, the atoms of O, S, and of metals, appear to exercise no influence. With regard to Cl, Br, I, they play the part of so many atoms of hydrogen: for instance, the three following metallic ethers should be considered to contain 16 atoms of hydrogen and not 15, for the constants k_t are a little higher than those of the compounds of As, P, &c., given above.

Formula.	S°obs.	d_t.	$t°$.	B.	Kt.
$C_6H_{15}ClSn$	209	1·428	8	39	27·32
$C_6H_{15}BrSn$	223	1·630	?	44	26·98
$C_6H_{15}ISn$	235	1·833	22	49	26·74

These are the experiments of Cahours.

I regret that space does not allow of my treating of corresponding temperatures and of the relative expansion of liquids, or of the application of this new Law to solutions.